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The extreme toughness of many spider silks depends (i) on the folding of the component proteins as much as (ii) on the hierarchical structures of the multi-protein threads. The spider's complex spinning process plays a major role in the folding and formation of the hierarchy of the silk threads. This is a process that is largely devoted to the controlled extraction of water. Our research project offered, firstly, an important approach towards a full understanding of silk structure-properties relationships by examining the underlying principles and design characteristics responsible not only for de-hydration of silk-feedstock into silk- fibre but also for re-hydration, i.e. the re-constitution and re-formation of silk-fibre into silk-feedstock.The second goal of our research was a better understanding of the use of silks in composites; to this effect we expanded our studies of analyzing silks integrated into natural composites by beginning exploratory investigations of interactions and integration with synthetic/commercial matrix materials.

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Understanding natural silks and their integration into composites

Final report for FA9550-09-1-0111 Feb 2012

Prof. **Fritz Vollrath,** ***Department of Zoology, University of Oxford, UK***

ABSTRACT: *The extreme toughness of many spider silks depends (i) on the folding of the component proteins as much as (ii) on the hierarchical structures of the multi-protein threads. The spider's complex spinning process plays a major role in the folding and formation of the hierarchy of the silk threads. This is a process that is largely devoted to the controlled extraction of water. Our research project offered, firstly, an important approach towards a full understanding of silk structure-properties relationships by examining the underlying principles and design characteristics responsible not only for de-hydration of silk-feedstock into silk-fibre but also for re-hydration, i.e. the re-constitution and re-formation of silk-fibre into silk-feedstock. The second goal of our research was a better understanding of the use of silks in composites; to this effect we expanded our studies of analyzing silks integrated into natural composites by beginning a exploratory investigations of interactions and integration with synthetic/commercial matrix materials.*

Overview: Silk offers a very attractive combination of strength and toughness coupled with environmentally benign processing. Significantly, the role of the hierarchical protein structure in controlling these properties is complex and on the whole not well understood although insights into the system are made increasingly illuminating due to work by a number of groups worldwide. These parallel studies also create problems as much confusion is generated by the occasional poor investigation. Nevertheless, it can be agreed that silks (and there are several thousand different basic types) would make extremely attractive models for synthetic fibres, if only their core construction principles could be sufficiently 'unravelled'. Providing fundamental (and real) insights into silk form-function relationships was the first of our goals in this research funded by the AFOSR; this goal perforce relies on basic science and is highly interdisciplinary and iterative. The second goal addressed an aspect of natural silks that has perhaps more immediate applicability: their integration into biological composites with often outstanding properties. After all, in Nature most wild silks are naturally integrated into complex composites that have highly evolved constructions, which follow construction principles that provide considerable novel insights.

Progress Summary:

While silks are generally considered to have superb material properties, there exists a huge range in mechanical behavior between different silks and even a specific silk can display huge variability. While commercial silk grading has known this for millennia, science has so far failed to make a clear-cut link between a silk's quality (e.g. its mechanical properties) and its internal structures. Yet the details of these links have significant implications for any attempts to 'improve on Nature' by selective breeding or trans-genic modification. Moreover, understanding these links will be crucial for any attempt to translate insights derived from natural silks by 'learning from Nature' into novel polymers with predictable properties. Some of our basic research over the last years focused on identifying molecular signatures and correlating them with molecular and morphological structure relying on natural diversity as well as modulations of processing procedures. Towards this goal we deployed a wide range of techniques, mostly using in-house equipment (some purchased with the support of the AFOSR) and often tuned in-house to maximum resolution and accuracy as we are typically using very small samples such as e.g. single fibres or dopes from a single silk gland.

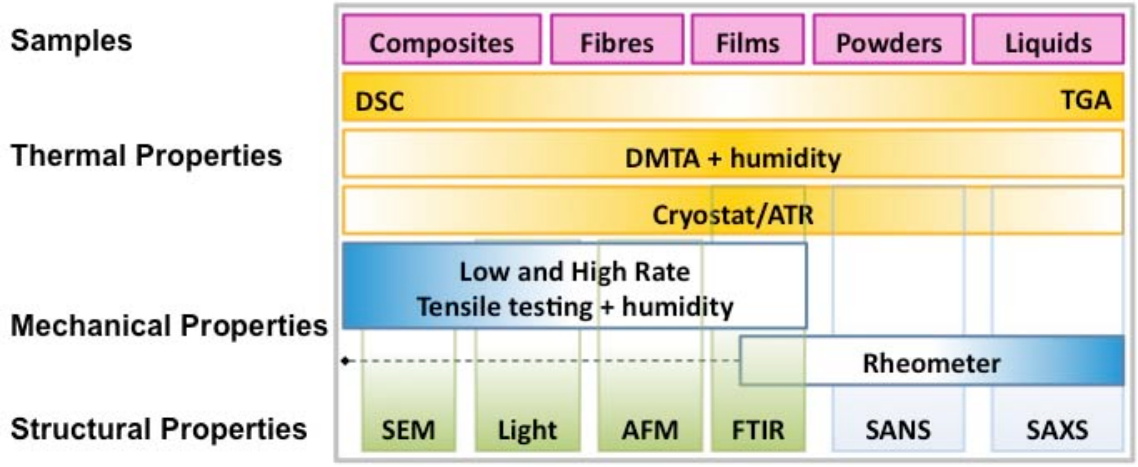

FIGURE 1 *Technical tools used in our analysis of silks in their various manifestations and transformations.*

A silk, by definition, has to undergo a spinning process and much of the material properties of a fibre rely on this extrusion process followed by post-draw. Consequently some of our basic research focused on the flow characteristics of native and non-native silks. This led us to the discovery that unspun natural silks behave like

melts while reconstituted silks are solutions or suspensions. This novel insight is turning-out to have significant implications for our understanding of silk process-structure-properties relationships.

Finally, part of the research team tested and deconstructed and re-tested natural as well as hand-made silk composites in order to better understand how the natural mechanical performance of silk fibres can be translated into high-performance fibre-reinforced composites.

During the duration of this funding period (2009-11) we have published xx research papers and xx reviews directly supported by the AFOSR (see references). The publications cover 3 research areas: silk-spinning, silk-fibres and silk-composites.

Fundamental Objectives

Our research in general aims to fully unravel the characteristics of benchmark silks, be they from an insect or a spider, by studying in detail the engineering properties of the final, post-draw fibres as they 'emerge' during the spinning and the associated hydration processes from the native polymer solution. Over the last few years we have focused on the de- and re-hydration properties of silks during spinning as well as the posibilities of re-constitution of silks in chaotropic agents. The new insights provide a foundation for future synthesis and application of silk-like polymers as exceptional engineering materials, such as super-tough fibre-reinforced composites.

Our fundamental research programme tested hypotheses on the natural folding of protein polymers and examined possiible mechanisms of their disintegration during natural exposure and during strong treatments aimed to break up the material for re-constitution.

Discoveries : Silks

To achieve the objective of gaining novel insights into silk structure-properties relationship, we used interconnected experimental work packages on a range of different silks to test a set of clearly formulated hypotheses about the role of structure on properties. These hypotheses and most of the relevant experimental and theoretical tools were developed in extensive screening trials by the Oxford Silk Group (see references on www.oxfordsilkgroup.com) and included empirical data collection as well as multiscale analysis and modelling in order to test and validate our hypotheses on structure-property relations. The viscoelastic analyses in this programme derived mainly from rheometry (some of that in collaboration with groups at Georgetown and Sheffield Universities) as well as in-house Dynamic Mechanical Thermal Analysis and FTIR Spectroscopy coupled with structural information on the protein polymers from

complementary parallel, collaborative investigations using techniques such as X-ray and Neutron scattering.

In order to develop a quantitative model for silk properties, in previous work we used the biological principle of energy management to help us refine an established polymer modelling approach called group interaction modelling : GIM uses a mean field potential function method for viscoelastic properties based upon energy storage and dissipation in interactions between characteristic groups of atoms in a polymer. For details see relevant publications (in list appended) but let me summarize in brief here. A reference purely elastic bulk modulus, B_e, is calculated from a potential energy-well of inter-group interactions. All the other components of the viscoelastic stiffness matrix (such as tensile and shear modulus) are the result of thermo-mechanical energy dissipation that reduces the modulus from the elastic upper limit. We were able to quantify the post-yield strain hardening to failure of the strongest silks, which is critical for their strength-toughness balance, and is the single most important differentiator between natural silk and synthetic polymers. New aspects of the model derived and published during the funding period are given in Porter & Vollrath and Vollrath & Porter [see details in references below] for silks as well as synthetic polymers. The combined set of models is able to predict the highly nonlinear mechanical properties of any polymer type as a function of temperature, strain, and strain rate in the form of analytical equations using a very small number of independently calculated structural parameters to describe composition and morphology. Thus, a model originally developed for simple amorphous polymers was adapted and extended by investigating silks in order to be reapplied more effectively to synthetic polymers. Clearly, this model (and its derivation) is an example of the benefits of biology-polymer dialogue and as such a suberb example of the important translational aspects of the grant. The AFOSR funding has allowed us to validate and refine these models for important new insights into silk properties that will be published in 2012.

Some important general principles were also formulated during this funding period by using the bio-GIM hypothesis validation approach to make prediction of silk properties both practical and physically meaningful in terms of structural features. First is the reduction of complex polypeptide structures simply into ‘ordered’ and ‘disordered’ fractions, since the more rigid ordered domains deform far less than the disordered domains; and the disordered domains can then be treated as relatively conventional amorphous viscoelastic polymer that is mainly responsible for energy dissipation, and therefore toughness. Second, the properties of silk can be fine-tuned by water that is active only in the disordered fraction, and acts in a similar way to conventional plasticiser in polymers. Water essentially binds specifically to polar groups in the silk and reduces the glass transition temperature of those segments. Since the accepted glass transition temperature, T_g, at about 200°C in dry silk is due specifically to polar amide-amide bonding, the thermal property of T_g is reduced by more water, and modulus and yield stress at any temperature are reduced in an easily quantified manner. Thus acting as a very effective property control.

Sensitivity to water is a key descriptor of silk properties. While some silks shrink and swell considerably when submerged in water, others shrink little or not at all. Silks that shrink tend to also respond to smaller changes in humidity, thus self-tuning the silk to environmental conditions. Importantly, these silks also tend to stiffen-up when re-dried and then show a significant drop in elastic modulus together with a significant increase in strain-to-failure. We have shown that these changes are directly linked to the loss of a meta-stable form of order on exposure to water, which is significant linked to the fraction of the disordering peptide group proline. Cyclical loading of these silks demonstrates that degree of order is reversible i.e. that it is, to some extent, plastic even in the finished fibre. This is due to the segments around proline being forced and then fixed by drying into a state of hydrogen-bonded order under strain. Water can then access the protein at the proline site and loosen the hydrogen bonds and relax the frozen-in strain for supercontraction.

Specific Outputs : Silk spinning and silk fibres

During this funding period we were able to further refine silk-dope rheometry to contribute significantly further towards our comprehension of the silk spinning process. First, Dr Holland from our group discovered that the feedstocks of two very different silks (silkworm and spider dragline) not only have very similar rheologies but also behave like typical molten polymers: an observation that opened the door to using techniques and models originally developed for the polymer sciences to study silk. This observation allowed us to conclude, from a fundamental perspective, that native silk polymer molecules behave like aqueous liquid crystal elastomers, which flow as 'strings' of coiled polymeric beads. Importantly, recent experimental work by Chris Holland in collaboration with Prof T. Ryan's Polymer Research Group at Sheffield University suggested a crucial refinement to our understanding. Through the novel imaging technique of shear induced polarized light imaging (SIPLI), we have quantitatively shown that the energy required for fibre formation (i.e. denaturation) in silk is *at least* an order of magnitude less than that of a typical polymer. We propose this massive energy saving is due to a native silk protein's unique interaction with it's bound water [2]. Hence we now consider native silk molecules and their associated water to be *a single processable entity*, an "aquamelt", a nanostructured state of biological matter - much like an individual polymer chain in a melt (FIGURE 2).

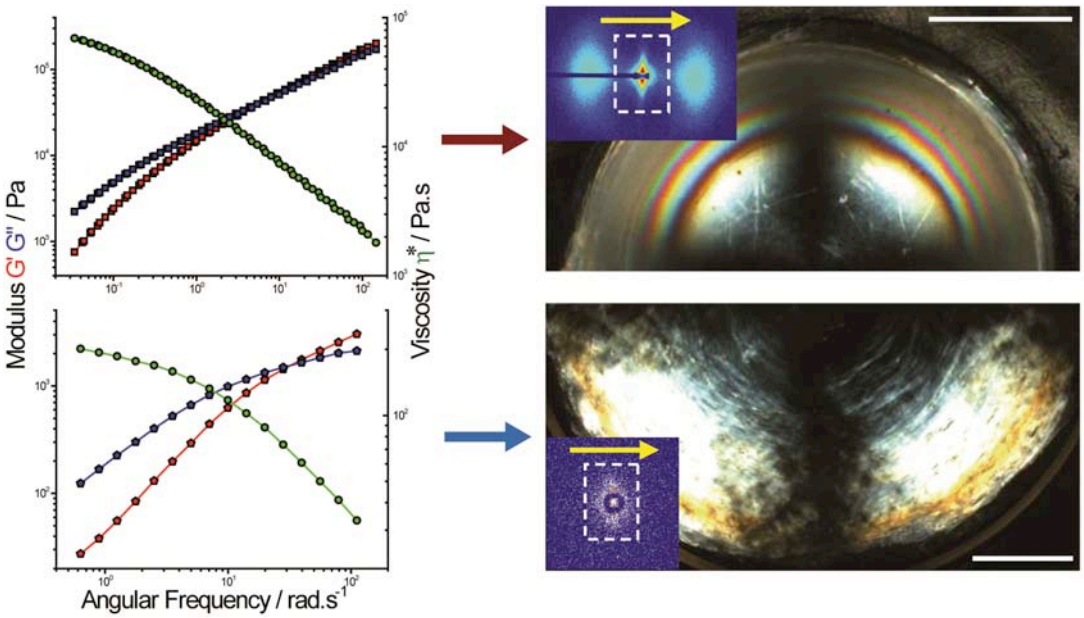

Figure 2. *Comparison of melt rheology (left) and shear-induced polarised light images, SIPLI (right) of HDPE (top) and silk (bottom). Rheological data represent HDPE master curves at 125°C (left top) and measurements of B. mori at 40°C (left bottom). Half-truncated SIPLI of polyethylene (right top, 125 °C, angular speed of the shear disk W = 0.333 rad/s, the gap between disks is d = 0.5 mm, t = 30s) and native silk dope (right bottom, 27 °C, W = 0.933 rad/s, d = 0.7 mm, t = 163 from B. mori). White scale line in the SIPLI scales to 5 mm. The insets show representative SAXS patterns corresponding to the areas forming fibres; the shorter side of the patterns scales to 0.05 $Å^{-1}$; the arrows show direction of the shear flow and the dashed squares indicate scattering originating from shear induced fibres.*

Silk's desirable properties originate from the development of a multiscale hierarchical structure produced during spinning, but until our studies (done by Chris Holland in collaboration with Jeff Urbach and Dan Blair from Georgetown University) little was known regarding the origin of the micro and nano-fibrils that are consistent and prominent features of spun fibres. This raised the important question: can shearing alone generate these filaments, or is further input and control by the physiology/morphology of the silk duct required? Combining confocal microscopy with rheology gave us unique insights into the direct connection between applied shear and the fibrillation of silk proteins in as close to in vivo conditions as currently possible. Our measurements demonstrate that unlike typical synthetic polymers, native silk proteins are able to spontaneously self-assemble, fibrillate and develop hierarchical structures upon controlled shearing, and that the shear induced fibrilogenesis is accompanied by dramatic changes in the rheological response. These observations suggest that natural spinning may be far less complex than previously assumed.

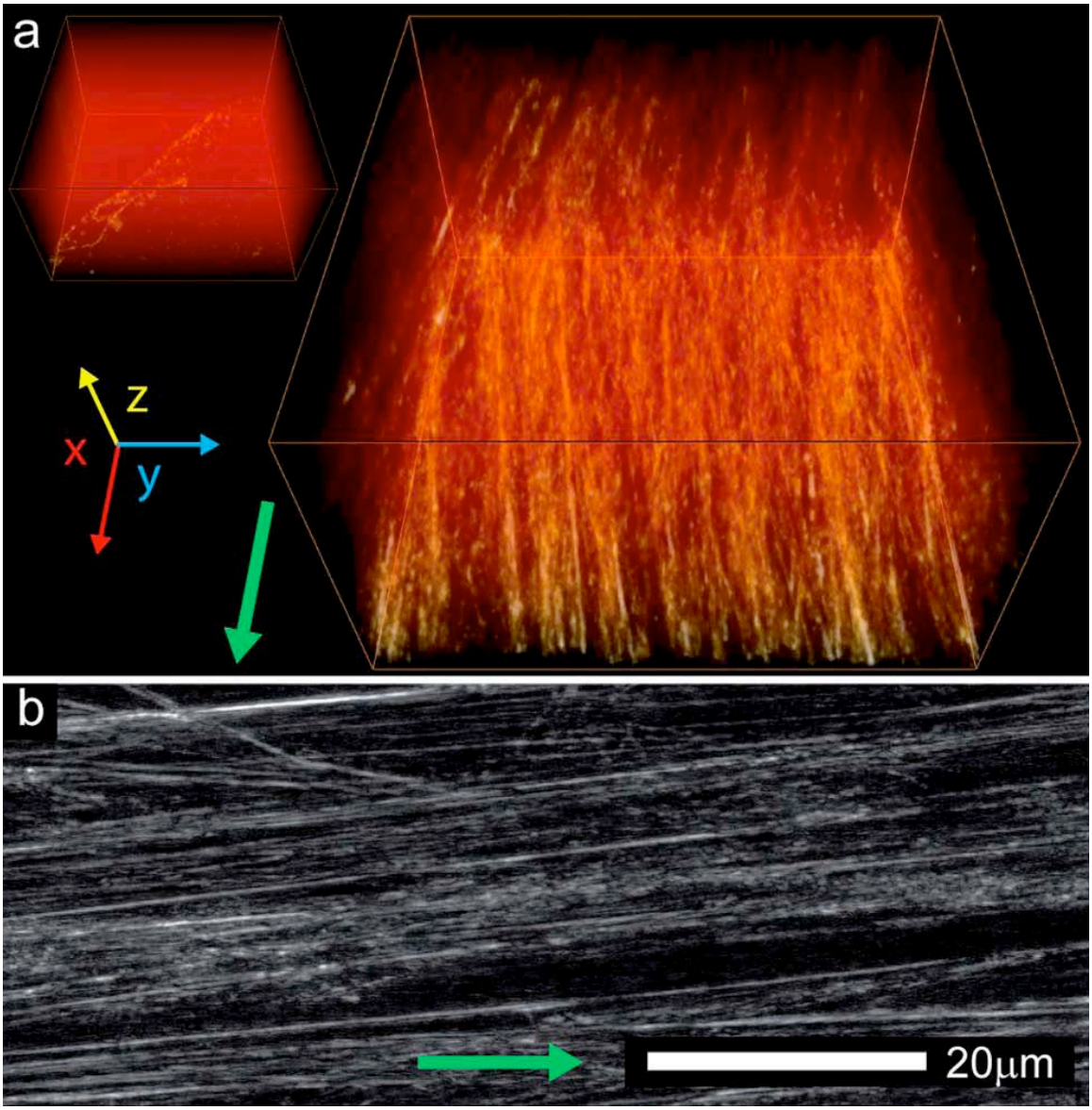

FIGURE 3 *Shear induced silk fibrillation visualised by confocal rheology. (a) 3-dimensional image of silk dope before (top left, inset) and after shear (bottom right). Bounding boxes are z stacks taken at 0.1mm intervals of size 77.5 _ 77.5 _ 38 mm (x,y,z). (b) Detail of fibrillation in a representative horizontal slice (x,y) of the sample taken at 5 mm above the lower coverslip. Green arrows represent the direction of shear. (from Holland, Urbach & Blair 2012)*

Discoveries : Composites

In addition to the work aimed to understanding not only structure-function relationships of fibres but also their natural diversity, we have also examined their integration into natural composites such as a spider's web or a silkworm's cocoon). In

such structures the processes of extrusion spinning (of the fibre) and growth by behaviour (building) are tightly integrated and have co-evolved material and structure over millions of years. The end products of such biological "design" processes can be high-complexity, composite materials and structures that are optimized for function and thus potentially very interesting models. In this part of our research we are studying in detail the integration of silk and natural resin into a range of composites. During this funding period we have focused on a variety of silkworm cocoons and deployed a mixture of experimental analysis and theoretical/engineering modelling. The insights thus gained allowed us to translate the knowledge gained from the empirical data and analysis of these natural composites to the design and creation of composites that mix natural fibres and synthetic components resins.

Specific Outputs : Composites

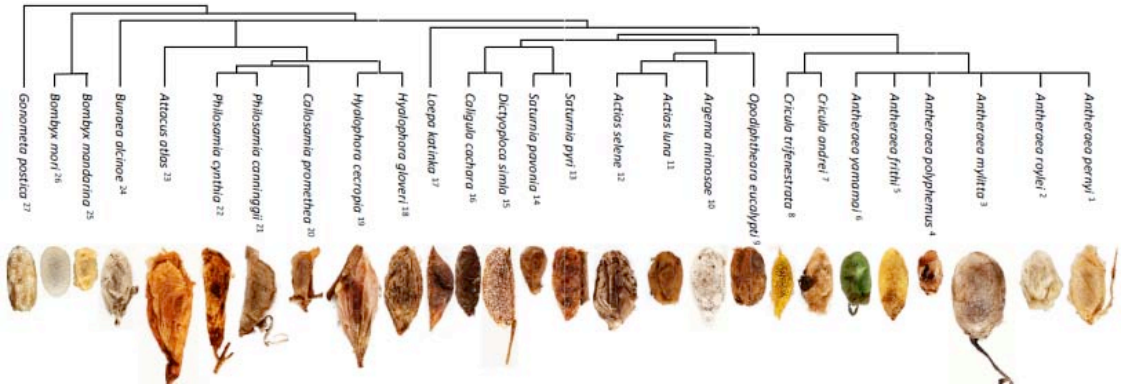

FIGURE 4 *Diversity of natural silk cocoon composites and their taxonomic relationships.*

The analytical tools used to examine fiber and composite mechanics are principally the mechanical testing of single fibre and composite sheet deformation coupled to thermal analysis and visual, inspection at very high resolutions. In particular, we examined the properties of silk fibres naturally embedded in native cocoons with special emphasis on the interaction of the fibres and their native resins e.g. sericins. This allowed us to study in considerable detail the fibre-fibre and fibre-matrix interfaces and interactions and construct formal models to examine the force of the interactions and the quality of the composites (FIGURE 5).

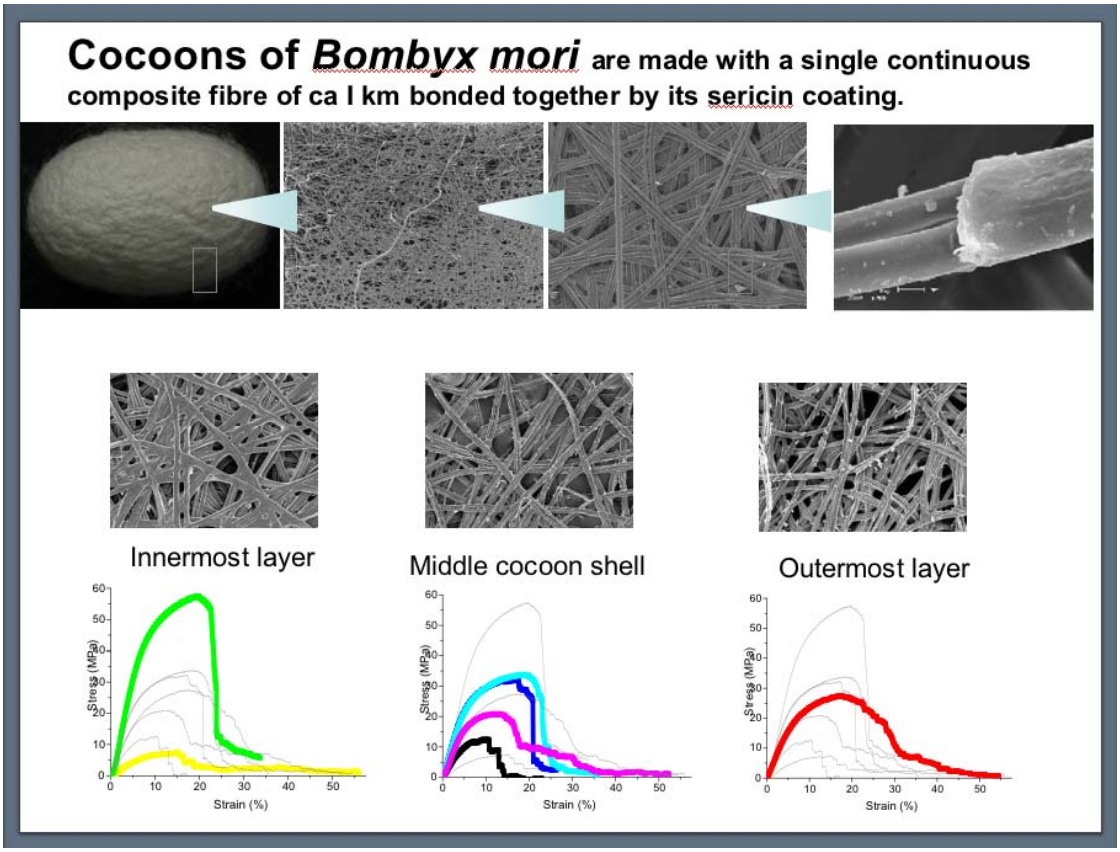

FIGURE 5: *Engineering of a natural composite and reduction to its components (from Chen, Porter & Vollrath, 2011).*

In the cocoon wall composites stress rises with a reducing modulus as strain increases and as the binding points between fibres are observed to break progressively. Importantly, after the stress peak, there is an abrupt decline, indicating a state deficient of the continuously bonded strain 'pathways' through the sample, which now is held together simply by entangled fibres. A physically realistic model for nonlinear mechanical properties of the cocoon walls in terms of the component materials and the composite morphology can be derived from those data. Importantly, the component material properties can be measured experimentally, as well as calculated using published structure-property relations. For our model, the key generic material parameters are a silk fibre's initial tensile modulus $Y_f \approx 9$ GPa and strength of about 400 MPa as well as a sericin matrix modulus of 3.5 GPa and failure stress of 130 MPa. We found that the initial elastic modulus of the cocoon walls is significantly lower than that of the fibres and binder due to bending (as spun by the gyrating silkworms) of the circular arcs of fibre with a radius of about 2mm . This set-up complies to the open-cell foam-model of Zhu, which, in turn, is an extension of the simpler Gibson-Ashby proportionality in density squared and shows how the elastic modulus of the composite is controlled by porosity.

Thus, (and in summary) our data on a variety of lepidopteran cocoons (FIGURE 3, 5) collected during this granting period suggest that damage through loss of connectivity of bonding between fibres gradually reduces the stiffness of the composite with increasing strain. Accordingly, we were able to adopt a pragmatic fracture mechanics approach and scale modulus linearly with the active fraction of bonded fibres that sustains load. In this radically simple connectivity model, we quantified the fraction of broken bonds by using an Arrhenius activation function in mechanical energy of deformation in strain, e, relative to an activation strain, e_a, squared, since elastic energy density is proportional to elastic strain squared.

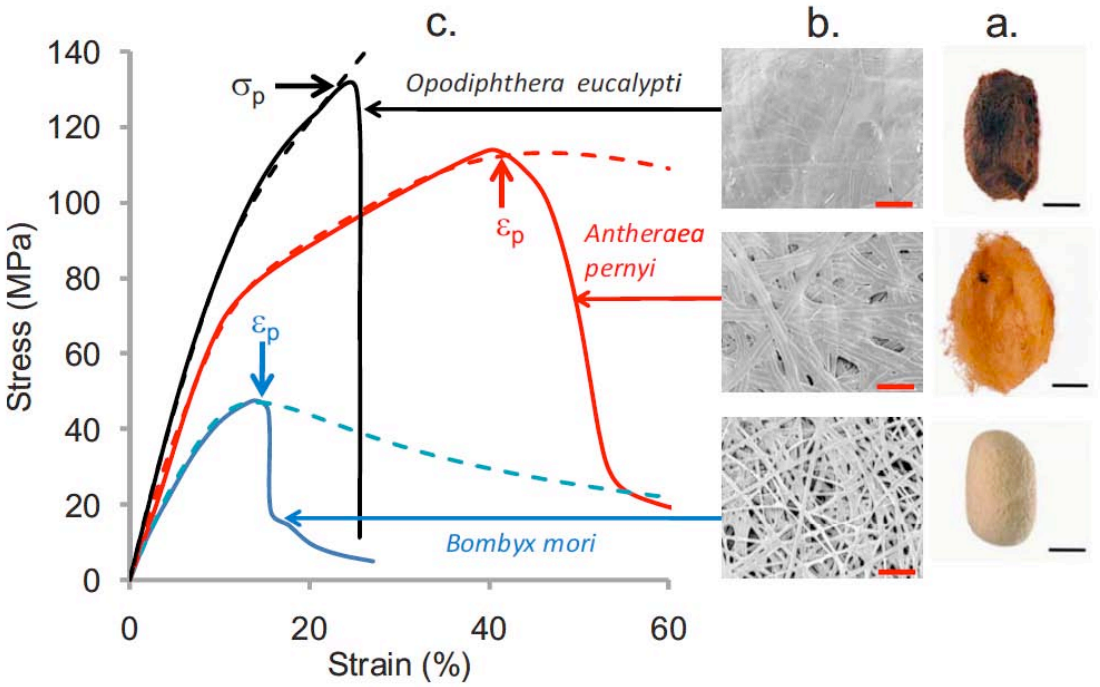

FIGURE 6: *a. The cocoons of Bombyx mori, Antheraea pernyi, Opodiphthera eucalypti (scale bar 10 mm) b. Typical bonded nonwoven structure of the middle layers of the cocoons (scale bar 200 μm). c. Stress-strain profiles for the cocoon walls, with solid lines showing experimental measurements and dashed lines as model calculations, with failure conditions shown as arrows in either stress (σ_p) or strain (ε_p); (from Chen, Porter & Vollrath, 2011).*

We conclude that the bonding connectivity in cocoon walls provides an excellent quantitative description of detailed nonlinear mechanical properties in a natural non-woven composite. However, such a model description has limited interest unless it has much broader applicability. We noted that a wide range of very different composite

materials have stress-strain profiles that are comparable to those of our cocoons, while noting also that current models for these materials are mathematically complex, quite narrow in scope, and largely empirical. Here, too, the main feature shared is the apparent control of mechanical properties by loss of connectivity of bonding between the component materials. Such loss occurs, either via fibre-fibre bonding for random fibre or via particle-matrix bonding for particulate composites.

We performed a similar analysis of the compressive properties of the cocoon walls perpendicular to the cocoon surface, and again used an established model to quantify properties in terms of the cocoon stucture and component properties. In addition, we measured the permeabilty of cocoons and showed their relation to structral parameters such as binder fractions (sericin and inorganic calcium oxalate crystals) and wall thickness. Finally, we used all the measured properties in engineering constitutive relations in finite element simulations (such as measured indentation trials, perhaps by pecking of a bird onto a cocoon) to show that the observations could be translated into useful engineering design tools.

Specific Outputs : Novel Discovery

The discovery of a novel silk production system in a marine amphipod provides insights into the wider potential of natural silks. The tube-building silk shrimp we studied (FIGURE 7) produces from its legs fibrous, adhesive underwater threads that combine barnacle cement biology with aspects of spider silk thread extrusion spinning.

FIGURE 7: *The corophioid amphipod silk shrimp Crassicorophium bonellii*

We characterised the filamentous silk as a mixture of mucopolysaccharides and protein deriving from glands representing two distinct types. The carbohydrate and

protein silk secretion is dominated by complex β-sheet structures and a high content of charged amino acid residues. The filamentous secretion product exits the gland through a pore near the tip of the secretory leg after having moved through a duct, which subdivides into several small ductules all terminating in a spindle-shaped chamber. This chamber communicates with the exterior and may be considered the silk reservoir and processing/mixing space, in which the silk is mechanically and potentially chemically altered and becomes fibrous. Further study of this independently evolved, marine arthropod silk processing and secretion system can provide not only important insights into the more complex arachnid and insect silks but also into crustacean adhesion cements. Thus this discovery of a 'first' i.e. a fully marine silk could lead to significant follow-up fundamental understanding of novel materials as well as possible applications of considerable potential.

Changes to the project as proposed : There were no changes.

Supported Personnel: Mr Gwilym Davies (PhD student, spinning technology), Ms Fujia Chen (PhD student, composite engineering), Dr Chris Holland (rheology), Prof David Porter (analysis), Prof Fritz Vollrath (overall leadership),

Collaborations: Prof Jeff Urbach and team (Georgetown University, Washington USA), Prof Toni Ryan and team (University of Sheffield), Prof Hannes Schniepp (University of William and Mary, Williamstown USA), Dr Lawrence Drummy (Air Force Research Laboratories (AFRL/MLBP, Materials and Manufacturing Directorate), Dr Katie Wahl (Naval Research Laboratory Tribology Section, Code 6176), Dr Tara Sutherland (CSIRO Canberra, Australia),

Interactions/Transitions: a wide range of invited and keynote lectures by all personal supported by this grant; in addition we had wideranging discussions with various companies about potential uptake of discoveries

Patents: 1 application submitted, 1 application in preparation

Publications this granting period 2009-2011 of work funded by FA9550-09-1-0111

Publications (30), Covers (4), Significant Press Coverage on 5 of the listed publications

2012 Holland C., Urbach J. S., Blair D. L. Direct visualization of shear dependent silk fibrillogenesis, *Soft Matter* **8** 2590-2594 access

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2011 Holland, C. Vollrath, F. Ryan, A.J. Mykhaylyk, O.O. Silk and Synthetic Polymers; Reconciling 100 degrees of separation *Advanced Materials* (online advance) access

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